Magnetic Fields at the Nuclei of Sn Impurity Atoms in Rare-Earth Ferromagnets

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The magnetic fields at the nuclei of Sn impurity atoms in Dy, Ho, Er and Tm rare-earth matrices at 7°K have been measured by means of the Mössbauer effect. The magnitudes of the fields were found to be equal to (185±5) kOe for Dy (Sn), (120±10) kOe for Ho(Sn), and (140±10) kOe for Er(Sn). Two magnetic field values associated with two magnetically inequivalent positions of the Sn atoms in the matrix, (105±8) kOe and (40±6) kOe, were obtained for Tm(Sn). It was found that the magnetic fields at the Sn nuclei in the rare-earth ferromagnets of the yttrium subgroup are proportional to the average over the first coordination sphere of the projection of the spin part of the magnetic moment on the total moment of the matrix ion. The temperature dependence of the magnetic field at the Sn nuclei in Dy and Ho was measured. Large deviations of the temperature dependence of the magnetic field from the Brillouin curves for the corresponding matrices were found. Possible mechanisms leading to such deviations are discussed.

SYSTEMATIC investigations of the magnetic fields at the nuclei of diamagnetic impurity atoms in metallic ferromagnets are of interest from different points of view. A large amount of experimental material has been accumulated on these fields for ferromagnets of the 3d-group (Fe, Co, Ni), a number of empirical regularities have been established, and different mechanisms, which explain qualitatively much of the data on the basis of the s-d interaction model, have been proposed[1-5]. However, the creation of a consistent theory of the magnetic hyperfine interaction in metals encounters well-known difficulties, and the problem, as a whole, remains unsolved at the present time.

The magnetic hyperfine interaction of diamagnetic impurities in rare-earth (RE) metals has been studied very little as yet. The difficulties of investigating this interaction for impurity atoms in RE metals are associated primarily with the exceedingly small solubility of most elements in these metals. Only recently have a number of papers appeared in which measurements of the magnetic fields at the nuclei of impurity atoms Sn in Gd[6], Sn in Er[7], Te and I in Gd[8], Cd in Gd[9], Sn in Tb[10], and Ag, In and Sb in Gd[11] were reported.

Campbell[12] proposed a model to explain the nature of the origin of the magnetic field at impurity nuclei in Gd. In this model, it is assumed that the sign of the conduction electron polarization in Gd is opposite to the sign of the conduction electron polarization in the 3d-ferromagnets. The experimental data[8] agree well with the predictions of this model; however, the results obtained in[9,11] require an appreciable change of one of the parameters of Campbell's model in order to attain satisfactory agreement with the experimental data. If, however, the model proposed in[2] is used, one can obtain fair agreement with experiment for nonmagnetic impurities in RE metals.

In the present work, we have measured the magnetic fields acting on the nuclei of Sn atoms in the Re metals Dy, Ho, Er and Tm. The measurements were performed by means of the Mössbauer effect at the Sn^{119} nuclei. The RE metals listed have a hexagonal closepacked crystal structure. The first coordination sphere about any site is formed by twelve atoms, of which six nearest neighbors lie in the basal plane and three atoms in each of the neighboring planes. At low temperatures, two magnetic phase transitions occur in these metals. At temperature Θ_1, a transition from ferromagnetism to antiferromagnetism (FM – AFM) occurs, and at a higher temperature Θ_2, a transition occurs from antiferromagnetism to paramagnetism. These temperatures for Dy, Ho, Er and Tm respectively are equal to: Θ_1 = 87, 20, 20 and 22°K, and Θ_2 = 179, 132, 80 and 56°K[13].

The magnetic moments in Dy in the FM regime are arranged parallel to each other as in classical ferromagnets. Ho and Er in the FM state possess a conical magnetic structure, and Tm has an alternating structure in which in four consecutive planes the moments point in one direction along the c-axis of the crystal, and in the next three planes in the other direction. In the AFM state, Dy and Ho have a spiral magnetic structure, in which the angle through which the magnetic moment vectors are rotated in the planes adjacent to the basal plane are increased from 26° at 90°K to 44° at 179°K for Dy and from 30° at 20°K to 49.5° at 133°K for Ho[13].

DESCRIPTION OF THE EXPERIMENT AND RESULTS OF THE MEASUREMENTS

Solid solutions of Sn (0.3 at.%), isotopically enriched to 86.9% Sn^{119}, in Dy, Ho, Er and Tm were prepared by fusion in an arc furnace in an argon atmosphere, with subsequent quenching. The metals Dy, Ho, Er and Tm, obtained from Giredmet (State Rare Metals Research Institute), were respectively 99.90, 99.80, 99.92 and 99.85% pure. Preliminary measurements were made with samples with a high Sn concentration. In these cases, however, additional lines appeared in the absorption spectra, caused by the presence of contaminant phases.

The absorbers for the Mössbauer experiments were prepared from alloy fillings, which were then deposited on a beryllium backing. $BaSnO_3$ containing the isotope Sn^{119m} was used as the source of γ-quanta. The measurements were performed on an electrodynamic spec-

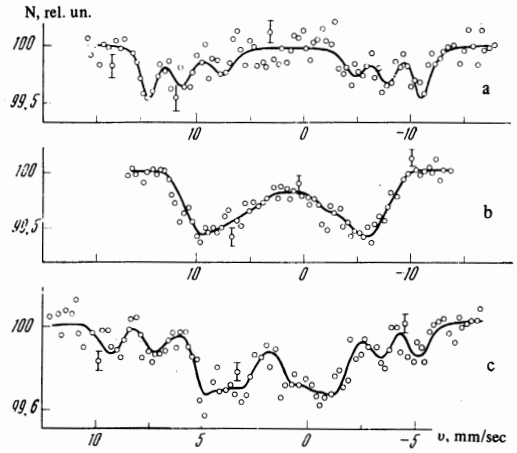

FIG. 1. Spectra of the resonance absorption of γ-quanta by nuclei of Sn^{119} impurity atoms in Dy (a), Ho (b) and Tm (c), measured at temperature 7°K. The speed of the source of γ-quanta is plotted along the abscissa, and the intensity of the flux of quanta in relative units along the ordinate.

trometer with an NTA-512 multi-channel analyzer. All the absorbers investigated by us at 300°K gave a single absorption line with half-width less than 1 mm/sec and with isomer shifts equal to (1.80 ± 0.07) mm/sec relative to $CaSnO_3$. With increase of the Z-matrix, an insignificant decrease of the shifts was observed; this, however, did not go outside the limits of the experimental errors. For the alloys Dy(Sn) and Ho(Sn), the Mössbauer absorption spectra were measured from a temperature of 7°K to the temperatures at which the matrices underwent transitions from the antiferromagnetic to the paramagnetic state, i.e., to the temperatures 179°K and 133°K respectively. The absorption spectra at temperature 7°K are shown in Figs. 1a and 1b. The magnitudes of the field H^{Sn}_{exp} at this temperature were found to be equal tp (185 ± 5) kOe for Dy(Sn) and (120 ± 10) kOe for Ho(Sn). The temperatures dependences of the field H^{Sn}_{exp} for Dy(Sn) and Ho(Sn) are depicted in Figs. 2a, b. It can be seen from these figures that the experimental points lie appreciably below the Brillouin curve for J = 15/2 in the case of Dy and for J = 8 in the case of Ho, and that the transition from the ferromagnetic to the antiferromagnetic state is not accompanied by any noticeable discontinuous change of the field at the Sn nuclei. The Dy and Ho matrices have similar magnetic structures in the antiferromagnetic regime, and the observed deviations, which pertain principally to this region, have a similar character.

In the Tm matrix (0.3 at.% Sn), the absorption spectrum for impurity Sn at 7°K gives two values of the magnetic field (cf. Fig. 1c). The magnitudes of these fields were found to be equal to (40 ± 6) kOe and (105 ± 8) kOe. An analysis of the magnetic structure of Tm[13] and of the possible location of Sn atoms in its lattice gives two possibilities for the magnitude of the magnetic field, each of which, in its turn, can give two fields of opposite sign. Since in the experiment an external field was not applied, only two values of the field were observed.

Measurements of the magnetic fields at the nuclei of Sn impurity atoms in Er were first made by Price and Street[7]; they obtained a value of the field equal to −(124 ± 4) kOe. Our observed magnitude of the field for Er(Sn) at 7°K is somewhat greater and is equal to (140 ± 10) kOe.

In the Table, we give the data available at present on the magnetic fields $H^{Sn}_{exp}(0)$ at the nuclei of Sn impurity atoms in Re metals of the yttrium subgroup.

	Gd	Tb	Dy	Ho	Er	Tm	
$H^{Sn}_{exp}(0)$, kOe	−329 ± 4	241 ± 6	185 ± 5	120 ± 10	140 ± 10; −124 ± 4	105 ± 6	40 ± 6
μ_1/μ_B	7	6	5	3.77	2,92	2	1
$H^{Sn}_{exp}(0)/\mu_1/\mu_B$, kOe	−47	40	37	31.8	47.9; −42.5	52.5	40

Note. μ_1 is the projection, averaged over the first coordination sphere, of the spin part of the magnetic moment on the total moment (in Bohr magnetons μ_B).

DISCUSSION OF THE RESULTS

In the rare-earth (RE) metals, the 4f-electrons, which are located in the "interior" of the electronic shell of the ion, are the principal carriers of magnetic moments localized at the lattice sites. The exchange interaction of the 4f-electrons with the conduction electrons, which have a largely s-character, is responsible for the ordering of these magnetic moments and induces polarization of the conduction electrons. The model of the s-f exchange interaction in RE metals is better founded than the s-d interaction model in the case of the 3d-transition metals.

In our interpretation of the magnetic fields at the nuclei of diamagnetic impurity atoms in Re metallic matrices, we start from the idea that these fields are induced by the polarized conduction electrons and not as a result of direct exchange, and the magnitude of the hyperfine magnetic field must be proportional to the conduction-electron spin density in the region occupied by the impurity. With the aim of simplifying, we postulate that the spin density is proportional to the conduction electron polarization, and that, for our study, effects due to the difference in behavior of electrons with oppositely directed spins play no part.

It is known that in the 3d-ferromagnets (Fe, Co, Ni) the magnetic fields at the nuclei of nonmagnetic impurity atoms are usually proportional, with good accuracy, to the atomic magnetic moment μM of the matrix. For the RE ferromagnets, the parameter equivalent to μM must be the projection of the spin part of the magnetic moment on the total moment, i.e., the quantity $2(g-1)J$, where J is the total moment of the trivalent ion of the RE element, and g is the Landé factor. The experimental results show that in RE ferromagnets with collinear ordering (Gd, Tb, Dy), the observed fields at the nuclei of Sn impurity atoms are indeed proportional to $2(g-1)J$ with good accuracy. For matrices with more complicated ordering, (Ho, Er, Tm), the magnetic structure is such that the moments of ions in different layers of the lattice are noncollinear (Ho and Er) or antiparallel (Tm), and the mean polarization of the conduction electrons must be proportional to the weighted vector sum of the moments, and not simply to the quantity $2(g-1)J$.

Postulating that it is the immediate neighborhood which plays the principal role in the formation of the magnetic field at the impurity nucleus, we obtain that the fields are approximately proportional to the average over the first coordination sphere of the projection of the spin part of the magnetic moment on the total moment μ_1, which is equal to $2(g-1)J$ for Gd, Tb and Dy, is less than $2(g-1)J$ for Ho and Er, and has two values for Tm. The absence of strict proportionality between $H^{Sn}_{exp}(0)$ and the quantity μ_1 (cf. the Table) is completely natural, since the collective contribution from more distant neighbors can differ markedly for matrices with different magnetic ordering.

The existence of two different magnetic field values at Sn nuclei in a Tm matrix demonstrates directly that the conduction electron polarization and the corresponding spin density depend on the details of the magnetic structure. In the case of the Tm matrix, a tin impurity atom can be situated in two magnetically inequivalent positions. In one position, the tin experiences a polarizing influence due entirely to Tm ions positioned in the same basal plane, while the exchange interactions with ions positioned in the immediate neighboring planes cancel each other. In the other position, the exchange interactions with the neighboring planes and in its own plane reinforce each other. Since an Sn atom has six nearest neighbors in its own plane and three nearest neighbors in each neighboring plane, one may expect that the field at the Sn nucleus will differ by a factor of approximately 2 for these two positions. In fact, the measured ratio is 2.6. The increase of the field by more than a factor of 2 could be connected with a number of reasons, e.g., with the fact that the interaction with the neighboring planes is a little greater than the interaction in the basal plane. But the very fact of this increase of the field makes it possible to conclude that the sign of the exchange interaction with ions of a neighboring plane is the same as the sign of the exchange interaction of ions in one plane. The same conclusion also follows from an examination of the data for the other matrices.

The temperature dependence obtained for the magnetic fields $H^{Sn}_{exp}(T)$ at the nuclei of Sn impurity atoms in Dy and Ho matrices (Fig. 2) shows that the mean value $\langle \sigma_Z \rangle$ of the conduction electron polarization close to an impurity falls off with increase of temperature faster than indicated by the corresponding Brillouin curves with J equal to 15/2 and 8. We shall consider the possible reasons for this deviation, using the molecular-field approximation. The magnitude of the polarization σ can be represented in the form

$$\sigma = 2\chi h_R / g\mu_B, \tag{1}$$

where χ is the electronic spin susceptibility, and

$$h_R = \frac{2}{g\mu_B}\sum_{R'} I_{RR'}\langle S\rangle_{R'} \tag{2}$$

is the molecular field at the point R, which gives the interaction equivalent to the s-f exchange; $\langle S\rangle_{R'}$ is the mean value of the spin of the ion at site R'; $I_{RR'}$ is the magnitude of the exchange interaction with electrons at the point R. The summation must be extended over all the lattice sites.

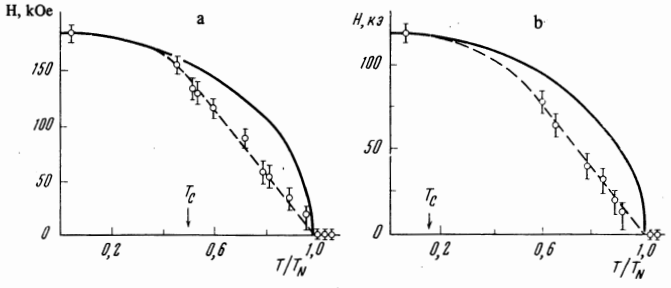

FIG. 2. Temperature dependence of the magnetic field at the nuclei of Sn impurity atoms in metallic Dy (a) and in metallic Ho (b). The solid curves are Brillouin curves for J = 15/2 and J = 8 respectively.

We first consider the temperature dependence of $\langle S_Z \rangle$ for ions of a matrix containing no impurity. This should be expressed by the Brillouin function $B_J(x)$, where $x = g\mu_B Jh_R/kT$, if the degeneracy of the state of the ion with total moment J is lifted as a result of the Zeeman interaction with the molecular field h_R. In the free-ion model, the magnetic field H^{4f}_{eff} at the nucleus of a RE ion is determined principally by the magnitude of $\langle J_Z \rangle$; therefore, the dependence of H^{4f}_{eff} on temperature should also be determined by the function $B_J(x)$:

$$\frac{H^{4f}_{eff}(T)}{H^{4f}_{eff}(0)} = \frac{\langle J_z\rangle_T}{\langle J_z\rangle_{T=0}} = \frac{\langle S_z\rangle_T}{\langle S_z\rangle_{T=0}} = \frac{B_J(x)}{B_J(\infty)}. \tag{3}$$

The contribution of the conduction electrons to this field is comparatively small (~100 kOe).

In Fig. 3, we give experimental values of H^4 $H^{4f}_{eff}(T)/H^{4f}_{eff}(0)$ for Dy nuclei in metallic dysprosium, obtained in paper[14]. It can be seen that the experimental points lie above the Brillouin curve for J = 15/2. We postulate that this deviation could arise mainly from the interaction of the Dy^{3+} ion with the crystal field. If this interaction is taken into account, the temperature dependence of $\langle J_Z \rangle$ will be determined by the function

$$\langle J_z\rangle_T = \Big(\sum_{J_z=-J}^{J}\mathscr{E}(J_z)\Big)^{-1}\sum_{J_z=-J}^{J} J_z\mathscr{E}(J_z), \tag{4}$$

$$\mathscr{E}(J_z) = \exp\Big(-\frac{g\mu_B J_z h_R + bJ_z^2}{kT}\Big),$$

which does not coincide with the function $B_J(x)$. The constant b characterizes the magnitude of the interaction with the crystal field. If we assume that the energy of interaction of the ion with the crystal field is approximately 0.2 of the energy of its interaction with the magnetic field, fair agreement is obtained between the experimental data and the calculation using formula (4) (cf. Fig. 3). The absence of complete agreement is not surprising, since we computed the simplest case of a combined interaction.

In our treatment, we assumed that the magnetization $\langle S_Z \rangle$ was the same for all atoms of the matrix. However, the presence of a nonmagnetic impurity should lead to a decrease of the magnetization of the neighboring atoms. The magnitude of this effect was calculated for a ferromagnetic matrix of cubic structure in the case of matrix atoms with spins $\frac{1}{2}$, 1 and

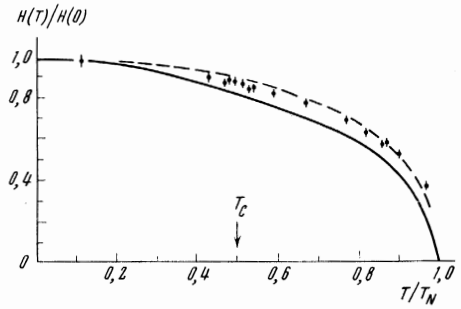

FIG. 3. Temperature dependence of the magnetic field for Dy nuclei in metallic Dy. The solid curve is the Brillouin curve for J = 15/2. The dashed curve is calculated from formula (4).

5/2 in[15], and for spin 7/2 in[16]. The calculations show (cf.[16]) that the magnetization decrease $\Delta\langle S_z\rangle_n = \langle S_z\rangle - \langle S_z\rangle_n$ is most marked for atoms of the first coordination sphere n = 1, while at a sufficiently large distance from the impurity, for $n \geq 7$, the magnetization $\langle S_z\rangle_n$ is equal to its unperturbed value $\langle S_z\rangle$. It is important to emphasize that these deviations $\Delta\langle S_z\rangle_n$ increase with temperature and reach a maximum at temperatures $\sim 0.9T_C$, and then fall sharply to zero at $T = T_C$. The maximum deviation of the magnetization, due to all the six closest spheres, approaches ~13%. The results of this calculation can be compared with the experimental data[6] on the fields at the nuclei of Sn impurity atoms in a Gd matrix (S = 7/2). In[6], the measurements were performed only up to temperatures $0.7T_C$. At this temperature, the measured value of the field at the tin nucleus is ~14% less than that expected from the Brillouin curve for J = 7/2, and the calculations give a decrease of ~9.3%. It follows from this comparison that the deviations in the temperature behavior of the fields at Sn nuclei in a Gd matrix may be due mainly to the effect of decrease of the magnetization of the neighboring Gd ions.

The fields we have measured at the nuclei of Sn impurity atoms in Dy and Ho matrices at $T = 0.7T_N$ have magnitudes 31% and 34% less than those predicted from the Brillouin curves for J = 15/2 and J = 8 respectively.

Theoretical calculations for the magnetization decrease due to a magnetic vacancy in a Dy matrix have not been performed, but, in our opinion, there are no reasons to assume that this effect will be much greater than in the case of Gd. Therefore, to explain such a substantial decrease of the fields at the nuclei of Sn impurity atoms in Dy, it is necessary to consider other possible effects: 1) the dependence on temperature of the exchange interaction $I_{RR'}$, and 2) the dependence on temperature of the spin polarization χ.

We now consider the first dependence.

For the molecular field h_R, in place of (2) we can write a simplified expression which takes into account only the contributions from atoms lying in the basal plane (interaction I_0), in the neighboring planes (interaction I_1), and in the next layers beyond the neighboring layers (interaction I_2):

$$h_R = \frac{2}{g\mu_B}[I_0 + I_1\cos\alpha - I_2\cos 2\alpha]. \quad (5)$$

The helical angle α between the magnetic moments lying in a given plane and in the neighboring plane is given by the known ratio

$$\cos\alpha = -I_1/4I_2. \quad (6)$$

The decrease of h_R arising from the change with temperature of the angle α only (we assume that the interaction $I_0 \sim L_1$ does not change with temperature) is found not to be large (10%). If we take into account the data for the dependence of I_1 and I_2 on temperature[17], we obtain for h_R a temperature dependence differing substantially from that observed for $H^{Sn}_{exp}(T)$. In this, we did not take into account the possible change of I_0 with temperature; therefore, the analysis of the effect of the assumed temperature dependence of the exchange interaction cannot be regarded as sufficiently reliable.

Turning to the dependence 2), we recall that the spin susceptibility of the conduction electrons, regarded as an electron liquid, is described by the expression

$$\chi = \mu_B^2\nu(\varepsilon_F)/(1+I). \quad (7)$$

Here, $\nu(\epsilon_F)$ is the density of states (per unit energy interval) for electrons situated at the Fermi surface in the metal, and I is a dimensionless coefficient characterizing the magnitude of the exchange interaction of the quasi-particles compared with their kinetic energy. In the literature, different mechanisms leading to a temperature dependence of the susceptibility χ have been considered. There are reasons for supposing that, with increase of temperature, there is an increase in the electron-electron scattering, which can lead to disordering of the spins. This effect should be manifested in the temperature dependence of the exchange interaction I. Another factor affecting χ arises from the dependence of the effective density of states $\nu(\epsilon_F)$ on temperature.

We note, finally, that the quantity χ in (1) is a tensor, and h_R can describe a spiral spin wave with wave-vector depending on temperature. Therefore, with change of temperature, anisotropic properties of χ may appear. To elucidate the role of the effects we have considered, further experimental and theoretical investigations are necessary.

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